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EVALUATION OF CATHODOLUMINESCENCE AS AN INDICATOR OF THERMAL MATURITY IN LIMESTONES.

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INTRODUCTION

Thermal history determinations form an important part of the evaluation of the hydrocarbon prospectivity of a sedimentary basin. Present methods of estimating palaeotemperatures rely on the analysis of organic matter and cannot always be applied to carbonate rocks, which are sometimes barren of suitable material. Whereas cathodoluminescence (CL) is widely used in studies of carbonate diagenesis to reveal textures invisible by polarizing microscopy (see Barker & Kopp 1991), its potential uses in palaeotemperature analysis have not previously been investigated.

The present study was undertaken to
(a) Compare natural calcite with synthetic material in terms of its response to thermal treatment
(b) Compare results from CL with those from conventional thermal maturation indicators.

PREVIOUS WORK

The chemical influences on CL are relatively well known in general terms (e.g. see Machel et al. 1991): Mn 2+ is the most important CL activator in natural carbonates and Fe 2+ is the most important quencher. There are sporadic references in the CL literature to a possible relationship between CL emission intensity in calcite and the thermal history of the rocks. For example, Medlin (1959), having noted a significant influence of annealing on subsequent thermoluminescence (TL) emission in synthetic calcite, mentioned that in natural calcite the effect was less marked. No details of the provenance of the natural calcite were given. Both Sommer (1972) and Nambi & Mitra (1978) attributed anomalies in the CL or TL of natural calcite to the effect of initial temperature of calcite growth or to subsequent heating by igneous intrusion. However, the influence of heat treatment of synthetic calcite or thermal history of natural calcite on CL emission has not been investigated systematically until now.

In order to investigate thermal effects on CL the author has carried out a program of room temperature synthesis of calcite followed by heating. Briefly, the results show that heating in the range 200°C to 500°C causes an increase in CL intensity (compared with equivalent unheated control material) of a factor of 1.5 to 3. Above 300°C as little as 2 or three hours is sufficient to induce the change in CL intensity: continued heating for longer times does not lead to a further increase in emission intensity. Below 300°C significantly longer heating time is required to induce the effect and greater changes are seen in longer heating experiments. At 100°C no measurable change in CL intensity occurs in experiments of up to 2400 hours duration, although data at this temperature are limited.

Fig. 1 shows the CL emission spectrum from an unheated synthetic calcite (activated by Mn^{2+}) and its heated equivalent. Typically the centroid of the Mn^{2+} emission peak lies in the range 600 to 615 nm and the half-width (full width at half the maximum intensity, FWHM) is around 90 nm. In the synthetic materials examined to date the centroid and FWHM do not change as a result of heating.

EXPERIMENTAL PROCEDURES

The samples were collected from Western Newfoundland by Drs S.H. Williams & E.T. Burden and their courtesy in making available their TAI (Thermal Alteration Index) and Ro% (vitrinite reflectance) data is gratefully acknowledged.

Of the approximately 40 samples studied by Williams & Burden (1992) only ten were suitable for the present study. Selection criteria were that the rock should consist of >95% carbonate on visual estimate and that the proportion of dolomite (visually estimated) should be low. This latter precaution was necessary because the CL emission from dolomite interferes with that from calcite, complicating the interpretation of the spectra. Five of ten grams of material was separated from each sample and hand crushed to approximately 5mm in size. A portion of each sample was crushed to 1mm grain size and divided into two aliquots, one to be subjected to heating, the other to be retained as a control. Heating experiments were performed in a vertical tube furnace through which Co_2 gas was passed to prevent decarbonation. Temperature was monitored with a thermocouple positioned within 3mm of the sample. All the experiments were performed at 400±5°C and the duration of heating was 24 hours.

Following heating the sample and control were crushed to a fine powder under methanol and mounted for CL measurements. Powdering allows the intensity to be averaged over many grains, thus minimising the effect of chemical zoning in individual crystals. Spectra were collected using a standardised set of CL operating

conditions: accelerating voltage 8kV; beam current 0.48 to 0.52 mA; beam dimensions 9mm x 5mm.

Spectra were obtained with a Nuclide Corporation ELM-2A Luminoscope coupled to a Gamma Scientific monochromator/controller combination wnich was scanned through the wavelength range 500 - 730 nm. Spectra were not corrected for the response of the photomultiplier all spectra were collected over the same wavelength range so such a correction is unnecessary. Replicate measurements were made on all samples. Electron bombardment in the CL microscope causes systematic losses of CL intensity as a function of bombardment time. The best strategy to minimise this effect is to collect spectra quickly and to change the field of view of the CL microscope for each spectrum collected.

Determinations of TAI and Ro% were taken from the report prepared for Mobil Canada by Williams & Burden (1992).

RESULTS

Table 1 summarises the results. The CL data are presented in terms of an intensity ratio I_H/I where I_H is the (integrated) CL intensity from the heated material and I is the (integrated) intensity from the (unheated) control. Table 1 is arranged in ascending order of the intensity ratio. An I_H/I value of 1 indicates no change in CL intensity, a value <1 indicates a decrease and a value >1 an increase in CL intensity following heating. In addition, measured values of TAI and Ro% from Williams & Burden are listed.

Figures 2 through 5 illustrate typical spectra taken from these samples: they may be compared with Fig. 1, which is from a synthetic calcite and its heated equivalent. The centroid position from all but one of the present samples lies in the range 605 to 612 nm, with the exception lying at 620 nm. FWHM values lie in the range 80-90 nm. Values for both these parameters are
within the range found for synthetic calcite, except that, in the latter material, centroids are always below 615 nm. Heating has no effect on the FWHM, again this is consistent with results for synthetic calcite. In two samples the centroid position measured on heated material differs from that of the control. In sample MOB1 (Fig. 2) the centroid shifted from 612 to 620 nm upon heating. In sample MOB8 (Fig. 4) the shift was from 611 to 605nm. This behaviour has not been seen in synthetic materials.

Figs. 2 through 5 illustrate the effect of heating on the CL spectra in both material with low CL intensity (samples MOB1 & MOB9: Figs. 2 & 3 respectively) and with relatively high intensity (samples MOB8 & MOB11: Figs. 4 & 5). Changes in CL intensity induced by heating range from -5% to +44% (Table 1) . None of the negative changes is significant, as indicated by the standard deviations on the I_H/I values (samples MOB4, MOB8 & MOB10). Small intensity increases (3 to 14%:samples MOB1, MOB6, MOB3 & MOB7) are statistically insignificant or of dubious significance but four samples (MOB2, MOB5, MOB11 & MOB9) showed significant increases in CL intensity after heating. The changes in CL intensity found in these natural calcites are much smaller than those found in synthetic material, in which intensity increases by a factor of two or more on heating under the same conditions (400°C, 24 hours).

Figures 6 & 7 illustrate the relationships between the intensity ratio (I_H/I) versus Ro% and I_H/I versus TAI, respectively. Error bars for I_H/I and Ro% are 1σ, from Table 1. Errors for TAI are not known. TAI data are not available for some samples but estimates were made for MOB1 & MOB9 based on results for samples from the same locality: the horizontal bars on Fig. 7 represent the range of TAI values for the locality. TAI and Ro% values for sample MOB11 are estimates communicated by Dr E. Burden.

It is clear that the CL data correlate only weakly with TAI and Ro% values. Fig. 6 suggests a weak positive correlation between I_H/I and Ro%. On Fig. 7, if the datum for sample MOB9 were ignored a case for a positive relationship could be made. The only justification for ignoring MOB9 is that the TAI value is an estimate for a sample locality, rather than a measurement on the sample used for the CL work.

DISCUSSION

Because of the relatively small number of samples studied by CL it is not possible to draw any conclusions of regional significance.

In terms of the development of CL as a tool for palaeotemperature estimation the results are encouraging in that they demonstrate that natural calcite responds to laboratory heating and must, therefore, be expected to respond to natural heating. However, comparison of the CL results with TAI & Ro% values is disappointing in that the relationships are poorly defined. In this context it is worth noting that the relationship between the established thermal maturation indicators TAI & Ro% and their dependence on temperature is subject to considerable uncertainty (see for example Fig. 7 of Williams & Burden 1992), perhaps because of inherent variations in the thermal response of material at relatively low temperatures.

Based on experience with synthetic material it was expected that calcite which had experienced palaeotemperatures above approximately 100°C would, when annealed in the laboratory, not show any increase in CL intensity. Conversely, it was expected that natural calcite which had never been above 100°C would behave more like calcite synthesised at room temperature, i.e. the CL intensity should increase significantly as a consequence of heating. On this basis the samples at the top of Table 1 would be identified as having been heated at above 100°C while those showing significant intensity increases (the last four samples in the table) should be those which have not been subjected to significant natural heating. As pointed out above, the relationships between I_H/I, TAI & Ro% are poorly constrained. However, if the interpretations given above are correct the relationships are exactly the reverse of those expected: the samples with the highest values of TAI & Ro%, indicating higher temperatures, are those which, on the basis of the CL results, have experienced only low temperatures.

CONCLUSIONS & SUGGESTIONS FOR FURTHER WORK

The differing responses of the samples to thermal treatment in the laboratory show that CL has definite promise as an indicator of thermal maturity. The Relationships between the CL results and conventional maturation indicators are subject to considerable uncertainty but it seems that the behaviour of natural calcite is more complex than that of synthetic calcite and requires more investigation.

Further work on a larger number of samples is required. It may be advantageous to estimate temperatures independently. Methods such as oxygen isotope analysis or fluid inclusion studies might be applied in favourable circumstances. It is suggested that a broader study of carbonates from the Northern Peninsula of Newfoundland be undertaken. Samples could be provided from existing collections by the author and others in CERR, supplemented by limited additional field work if necessary.

REFERENCES

Barker, C.E. & Kopp, O.C. (Eds) 1991. Luminescence Microscopy and Spectroscopy: Qualitative and Quantitative Aspects. SEPM Short Course 25, Dallas, Texas.

Machel, H.-G., Mason, R.A., Mariano, A.N., Mucci, A. 1991. Causes and measurement of luminescence in calcite and dolomite. In: Barker & Kopp, op. cit.

Medlin, W.L. 1959. Thermoluminescent properties of calcite. Journal of Chemical Physics, 10, p451-458.

Sommer, S.E. 1972. Cathodoluminescence of carbonates, II. Geological applications. Chemical Geology, 9, p275-284.

Nambi, K.S.V. & Mitra, S. 1978. Thermoluminescence investigations of natural calcite crystals of differing genesis. Thermochimica Acta, 27, p6l-67.

Williams, S.H. & Burden, E.T. 1992. Thermal Maturity of Potential Paleozoic Source Rocks in Western Newfoundland. Report submitted to Mobil Canada, February 1992.

FIGURE CAPTIONS

Fig. 1 CL spectra from a synthetic calcite containing 160 ppm Mn. Heating has increased the CL integrated intensity by a factor of approximately 2.

Fig. 2 CL spectra from a natural sample with a weak CL signal which did not respond to annealing. Note the shift in centroid consequent on heating, this is unusual & has not been seen in synthetic material.

Fig. 3 CL spectra from a natural sample with a weak CL signal which increased by approximately 44% following annealing.

Fig. 4 CL spectra from a natural sample with a relatively strong CL signal which remained unchanged by heating. Note that the shift in centroid is opposite in direction to that shown in Fig. 2.

Fig. 5 CL spectra for a natural sample with a relatively strong CL signal and which was changed significantly (35%) by annealing.

Fig. 6 Intensity ratio (I_H/I) versus vitrinite reflectance (Ro%) .

Fig. 7 Intensity ratio (I_H/I) versus Thermal Alteration Index (TAI).

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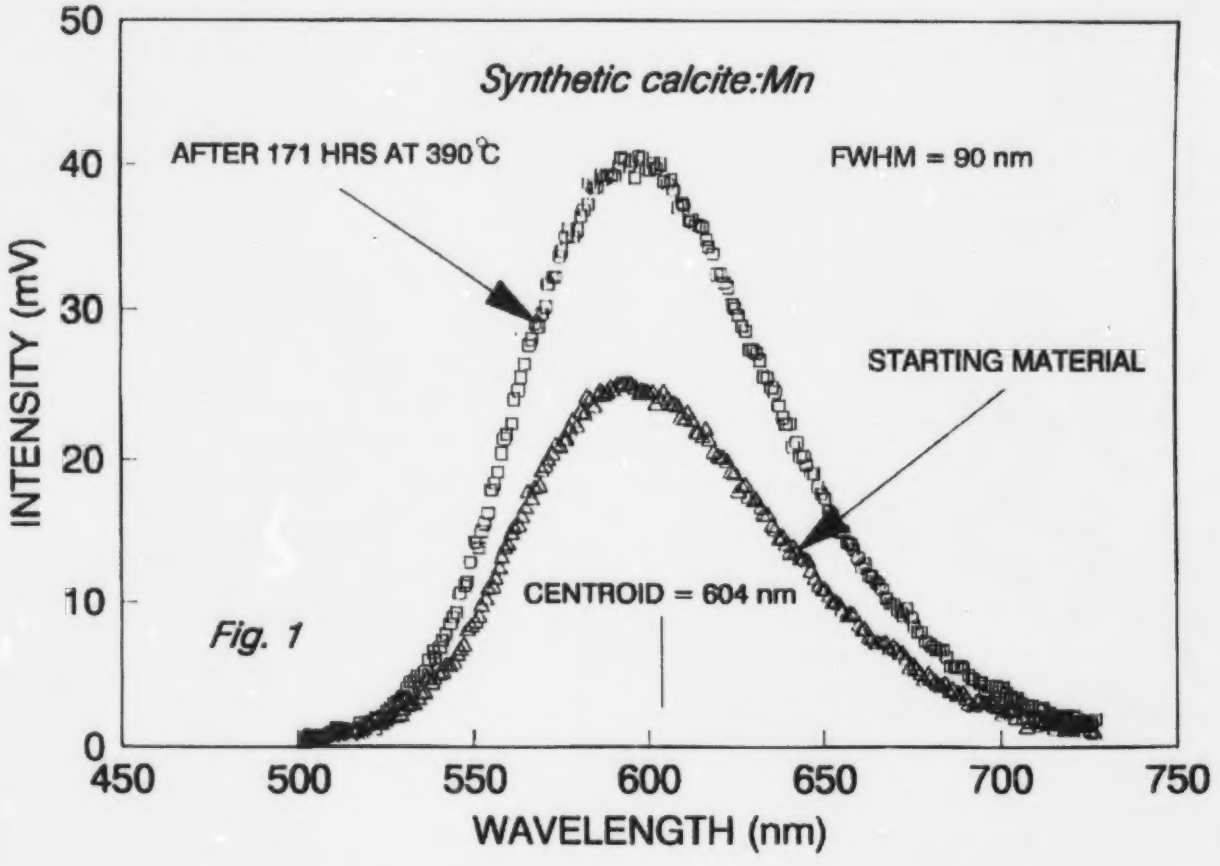
Synthetic calcite:Mn
AFTER 171 HRS AT 390°C
FWHM = 90 nm
STARTING MATERIAL
CENTROID = 604 nm
INTENSITY (mV)
WAVELENGTH (nm)
0
10
20
30
40
50
450
500
550
600
650
700
750

Fig. 1

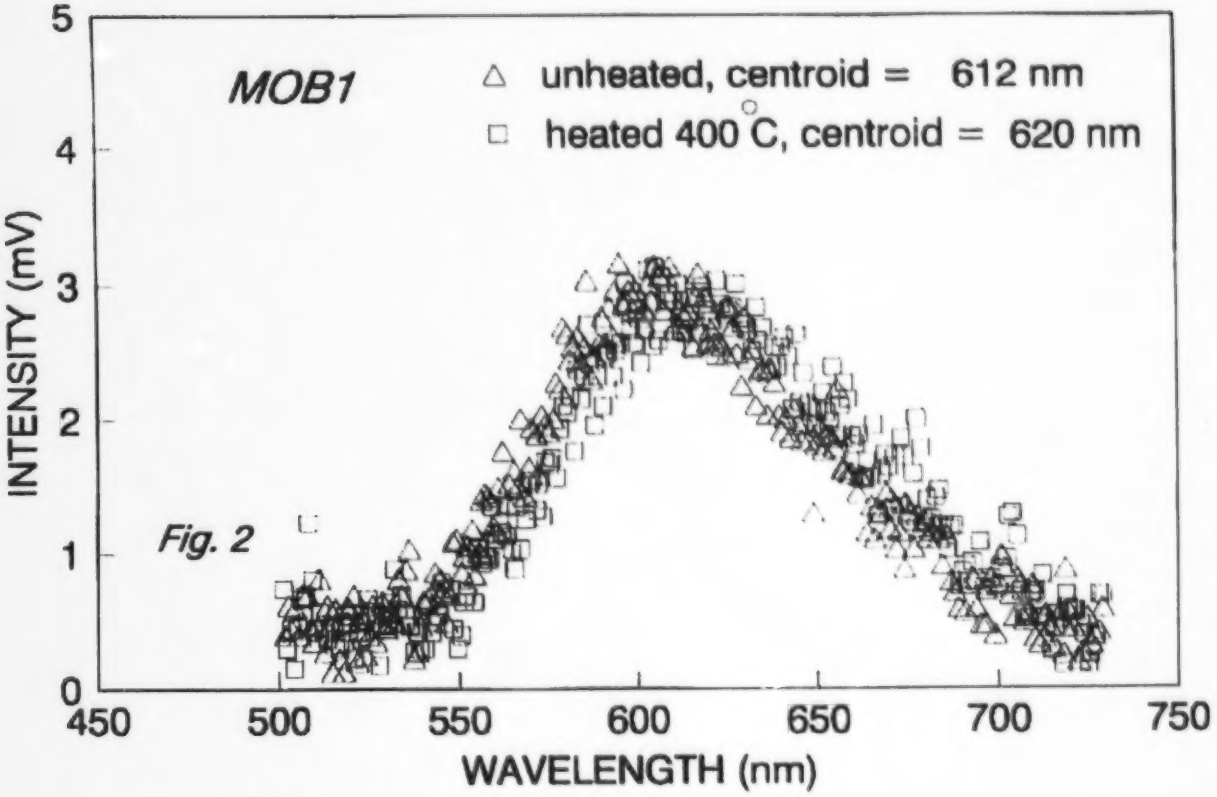
MOB1
△ unheated, centroid = 612 nm
□ heated 400 °C, centroid = 620 nm
INTENSITY (mV)
WAVELENGTH (nm)
0
1
2
3
4
5
450
500
550
600
650
700
750

Fig. 2

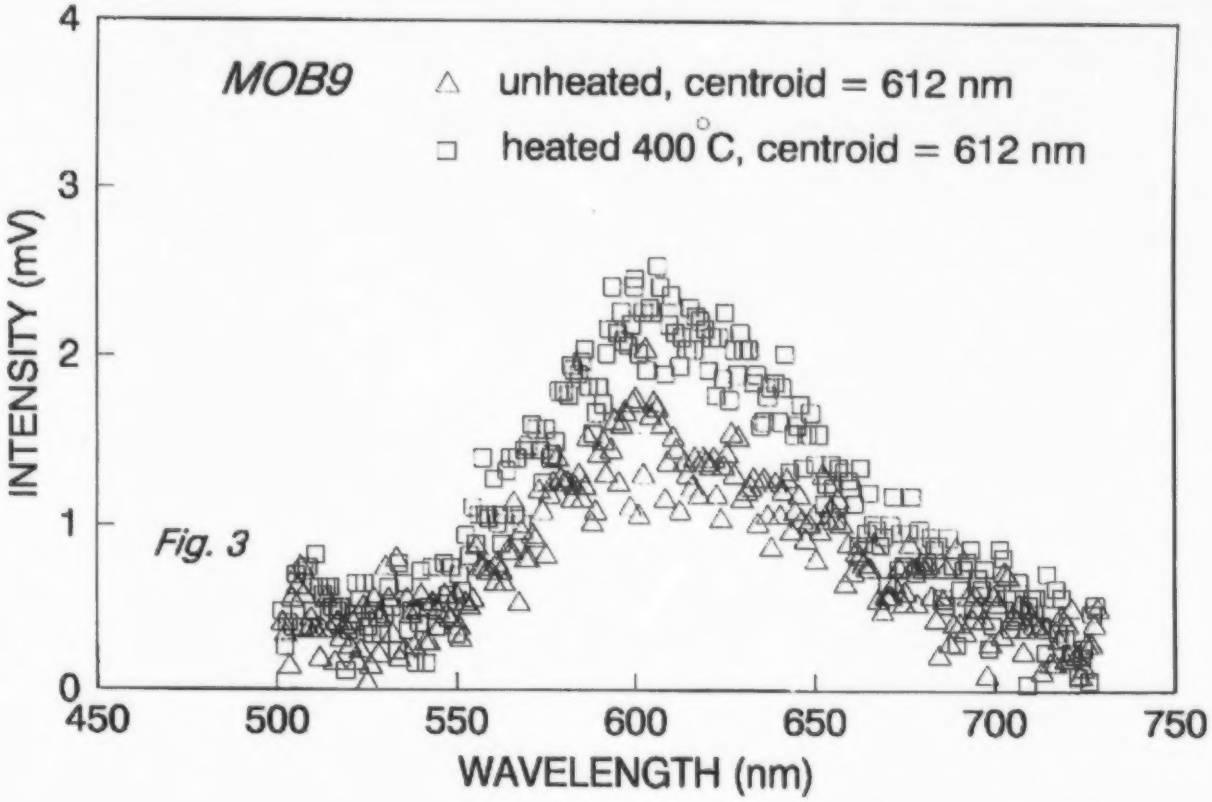
MOB9
△ unheated, centroid = 612 nm
□ heated 400°C, centroid = 612 nm
INTENSITY (mV)
WAVELENGTH (nm)
0
1
2
3
4
450
500
550
600
650
700
750

Fig. 3

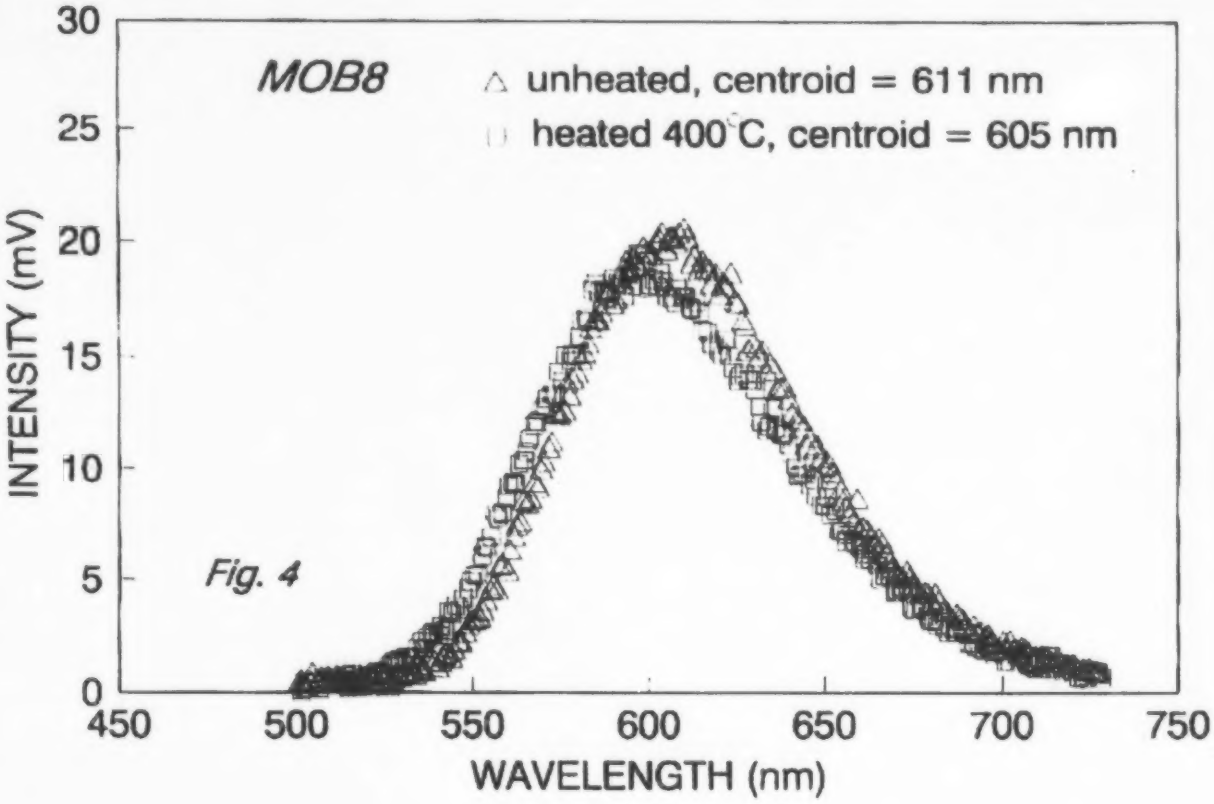
MOB8
△ unheated, centroid = 611 nm
□ heated 400°C, centroid = 605 nm
INTENSITY (mV)
WAVELENGTH (nm)
0
5
10
15
20
25
30
450
500
550
600
650
700
750

Fig. 4

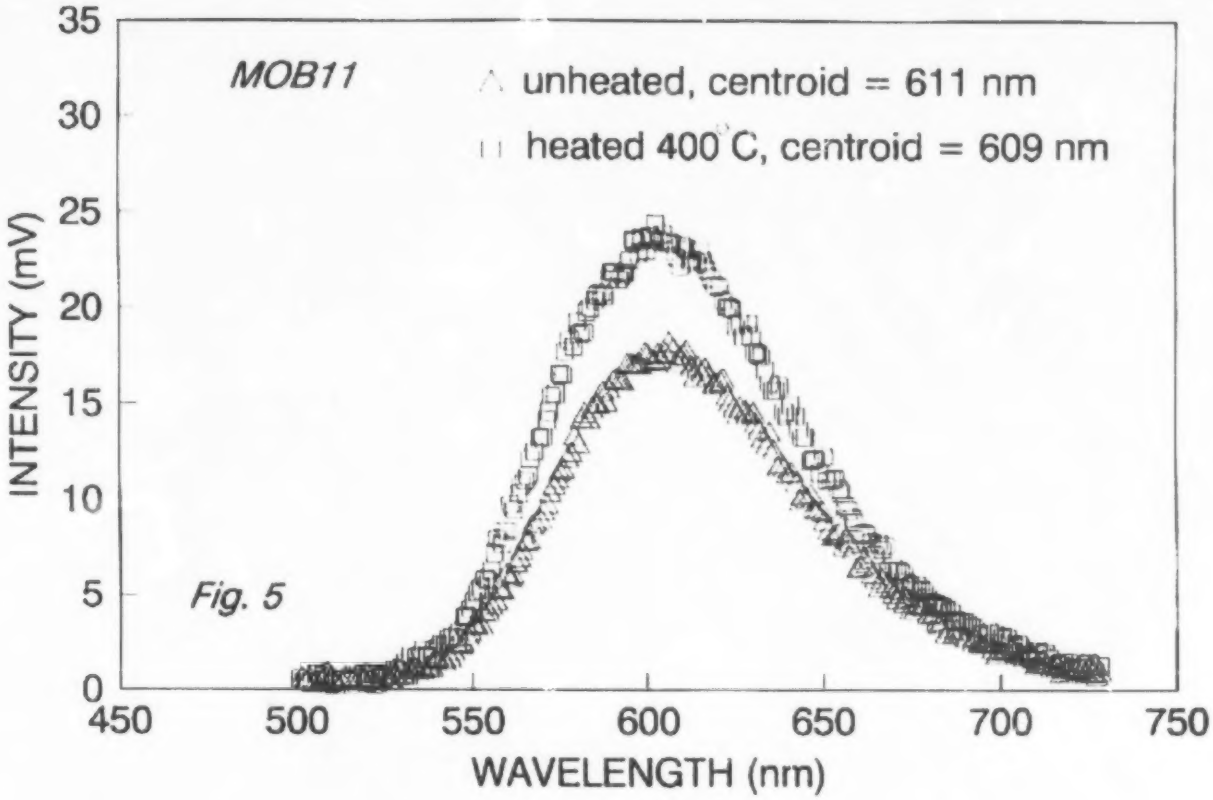
MOB11
unheated, centroid = 611 nm
heated 400°C, centroid = 609 nm
INTENSITY (mV)
WAVELENGTH (nm)
0
5
10
15
20
25
30
35
450
500
550
600
650
700
750

Fig. 5

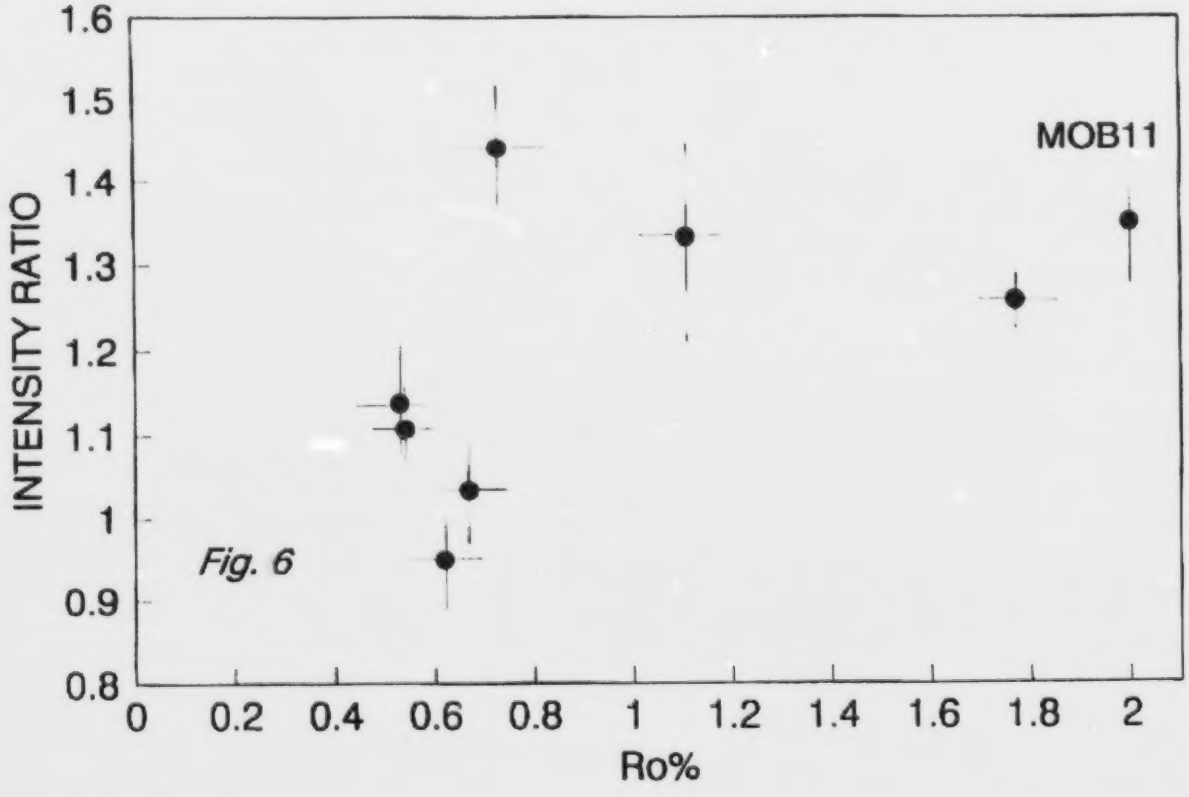
MOB11
INTENSITY RATIO
Ro%
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2

Fig. 6

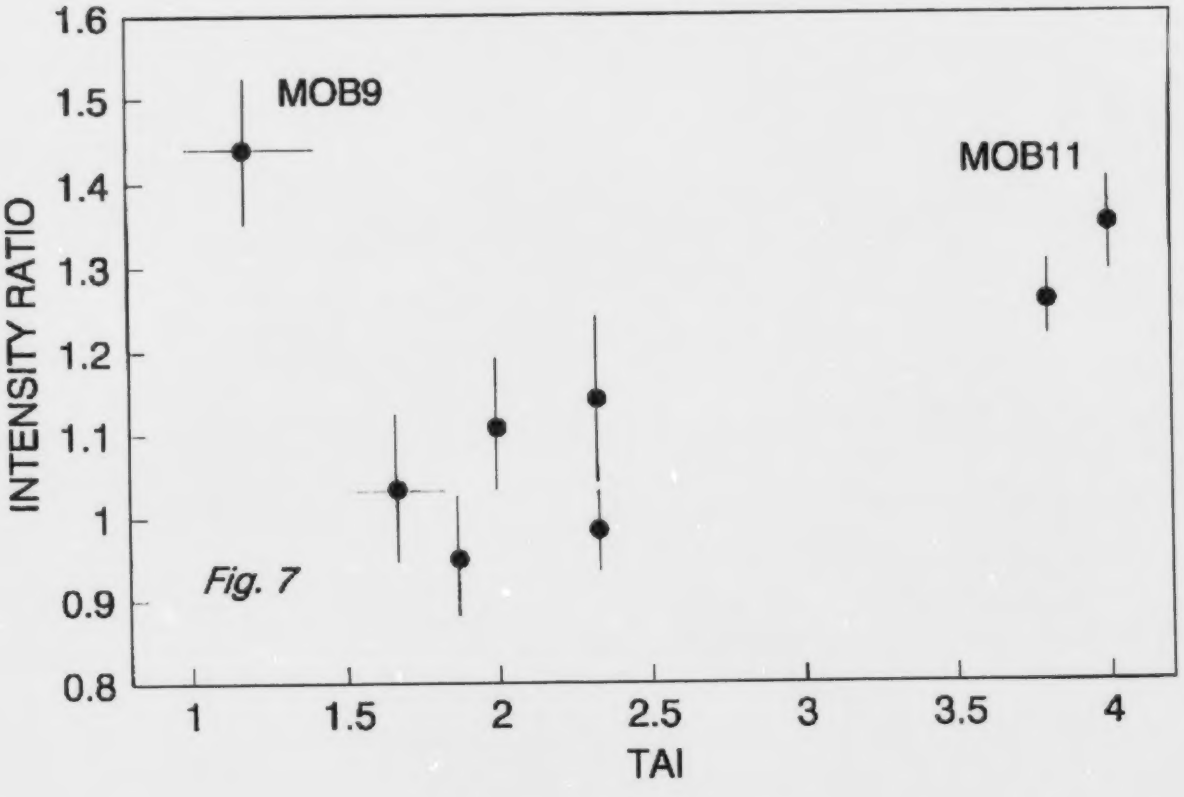
MOB9
MOB11
INTENSITY RATIO
TAI
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
1
1.5
2
2.5
3
3.5
4

Fig. 7